

PETC's ON-SITE NATURAL GAS CONVERSION EFFORTS

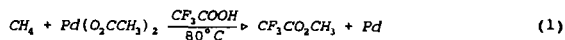
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ABSTRACT Investigation of the direct conversion of natural gas (i.e., methane) to transportation fuels has been an ongoing effort at PETC for over 10 years. Two of our recent areas of interest have been the oxyhydrochlorination (OHC) of methane and the oxidation of methane by organometallics. The OHC reaction is a two-step process in which methane, hydrogen chloride, and oxygen are reacted to produce methyl chloride. The methyl chloride is then reacted over a zeolite to produce gasoline-range hydrocarbons. Another area of interest, the oxidation of methane with organometallics, has produced interesting results. The reported reaction occurs between methane (at 800 psig, 5.52 MPa) and palladium(II) acetate in trifluoroacetic acid at 80°C. The product, methyl trifluoroacetate, is readily hydrolyzed to produce methanol and trifluoroacetic acid.

INTRODUCTION A significant portion of proven global natural gas reserves are in remote areas of the world where transporting the gas to market is not economically feasible. The conversion of natural gas to liquid fuels would permit facile storage, transportation, and distribution of a higher energy density fuel using established technologies and distribution networks. Key to a natural gas conversion process is the conversion of methane, the major component. The Pittsburgh Energy Technology Center (PETC) has been involved in this effort. Recent research has led to a two-step process for the conversion of methane to gasoline-range hydrocarbons¹⁻⁴. Methane, oxygen, and hydrogen chloride react over an oxyhydrochlorination (OHC) catalyst in the first step to produce predominantly chloromethane and water. In the second step, the chloromethane is catalytically converted to higher hydrocarbons, mainly in the gasoline (C₄-C₁₀) boiling range, by a pentasil-type zeolite such as ZSM-5.

Reports have appeared in the literature describing the use of organometallic complexes to selectively oxidize methane.^{5,6} Investigation of one of these reaction schemes in our laboratory has produced interesting results.⁷⁻⁹ Our research effort was an extension of work reported by Sen and coworkers.⁷⁻⁹ The reported reaction occurs between methane (at 800 psig 5.52 MPa) and palladium(II) acetate in trifluoroacetic acid at 80°C (Equation 1). The product, methyl trifluoroacetate, is readily hydrolyzed to produce methanol and trifluoroacetic acid.



OHC REACTIONS:

EXPERIMENTAL The catalysts for the OHC reaction were prepared by sequential deposition of the appropriate metal chlorides, or their precursors, in non-aqueous solvents onto a fumed silica support. The catalysts were tested for OHC activity under a predetermined set of conditions and compared to the copper/potassium/lanthanum chloride catalyst. All reactions were conducted in a 0.5-in (1.27-cm) o.d. x 7-in (17.8-cm) quartz up-flow reactor tube. A blank catalyst was prepared under identical conditions to those used for the metals but only containing potassium and lanthanum chlorides on the silica support. The catalysts were activated in a stream of hydrogen chloride at 300°C prior to testing. Composition of the catalysts, by weight, is given in Table I. An on-line mass spectrometer was used to determine conversions and product yield.

RESULTS AND DISCUSSION Table II lists reactant conversions under conditions utilized for the copper/potassium/lanthanum chloride catalyst and Table III lists the normalized carbon product distribution. With the exception of the cobalt catalyst, all catalysts exhibited a lower conversion of methane and lower methyl chloride production than did the copper. Temperature profiles for all the catalysts were performed along with lifetime studies for the copper and cobalt catalysts. Reactant conversion and product distribution remained constant during the 400 hours on stream for both the copper and cobalt catalysts.

Differences in activity of the copper and cobalt OHC catalysts have been observed depending on the person in our laboratory who prepared them. The lower activity catalysts result in both lower conversions and poorer selectivity for chloromethane. In an effort to better understand these observations, the catalysts were analyzed for structural differences.

Preliminary scanning electron microscopic (SEM) examination of two supported copper OHC catalyst samples showed some differences in morphology and segregation of Cu, Cl, La, and K. The overall elemental compositions of the two samples were similar, as shown in the energy dispersive spectroscopy (EDS) spectra, however, the SEM micrographs displayed a difference in particle size. The more active catalyst exhibited a finer particle texture with fewer large copper-potassium chloride needles. Identical results were observed for two samples of the Co-OHC catalyst that exhibited different OHC activities.

X-ray diffraction (XRD) studies performed on the two Cu-OHC catalyst samples utilizing a Cu-K_α radiation exhibited some differences. The most significant

was at 2 θ angles of 11.6 and 6.05 degrees. The more active catalyst exhibited intensities at these positions which were greater by a factor of 2 and 5, respectively. Upon exposure of the catalyst sample to humid air the 2 θ peak at 6.05 degrees disappeared.

CHLOROMETHANE CONVERSION REACTIONS:

EXPERIMENTAL All reactions were conducted in a 0.5-in (1.27-cm) o.d. x 7-in (17.8-cm) quartz up-flow reactor tube. The ZSM-5 was obtained from Mobil Oil Corporation in the ammonium form with a silica-to-alumina ratio of 70:1. The ammonium form was converted to the acid form by calcining in air at 538°C for 16 hours. Typically, 1.0 g of ZSM-5 zeolite was supported on a deactivated quartz-wool plug, heated to 350°C, and exposed to methyl chloride or mixtures of chloromethanes approximating the composition produced in the OHC reaction. Flows of reactants were selected to maintain a weight hourly space velocity (WHSV) of 1. An on-line mass spectrometer was used to determine conversion.

The liquid condensate was collected in an ice bath during the experiments and was analyzed by utilizing a 100 m X 0.25 mm i.d. fused silica column coated with a 0.5 μ m film of 100% methylpolysiloxane (Petrocol DH) and a helium carrier gas having an average linear velocity of 31 cm per second at 30°C. The low boiling, low molecular weight products not condensed in the ice bath were determined by directly sampling the reactor effluent product vapor and analyzing it by gas chromatography using a 50 meter X 0.32 mm porous layer open tubular (PLOT) column containing Al₂O₃/KCl¹⁰. The identifications made in this manner were confirmed by combined GC-MS and/or GC-FTIR. GC-MS was performed using a Hewlett-Packard 5988A system equipped and operated with the same chromatographic column and conditions as above. Further confirmation of these identifications was obtained by combined GC-FTIR using a Digilab FTS 65 GC/C 32 system equipped with a Hewlett-Packard 5880 GC and the same column mentioned above utilizing identical chromatographic conditions. The GC-FTIR experiments were performed at Digilab in Cambridge, Massachusetts.

RESULTS AND DISCUSSION In a typical experiment, chloromethane conversion varies from 98.5% to 100%. Over 240 compounds have been analytically separated in the reaction mixture and individual compounds constituting about 90 weight percent of the products have been identified. The liquid condensate did not contain significant amounts of the low boiling, low molecular weight products formed during the reaction. These compounds were determined in a separate experiment by sampling the reactor effluent immediately after exiting the reactor and analyzing them by using on-line gas chromatography employing an alumina PLOT column.

At 360°C, 1,2,4-trimethylbenzene is a major organic product formed in the reaction and constitutes about 45 weight percent of the total liquid product. Tetra- and pentamethylbenzenes are also found in the product but in substantially lower amounts.

A few weight percent (~1%) of the products were identified to contain chlorine. A large portion of these are 2-chloroalkanes. These are postulated to be formed by Markovnikov addition of hydrogen chloride, an elimination product of chloromethane conversion, to terminal olefins. The addition may occur in the reactor or down stream of the reactor in a hot zone.

ORGANOMETALLIC METHANE REACTIONS:

EXPERIMENTAL All reactions were conducted in a sealed, 0.5-in (1.27-cm) o.d. x 12-in (30.5-cm) silica-lined stainless-steel batch reactor. The reactor was lined by Restek, Inc. Total volume of the reactor system was <35 mL. In order to reproduce the literature results, experimental conditions were the same as those reported by Sen and coworkers.⁷

The reactor was rinsed with 5.0 g (3.3 mL) of dry trifluoroacetic acid, dried in a vacuum oven at 110°C, backfilled with dry nitrogen, and charged with reactants. Typically, the charge consisted of 0.15 g of palladium(II) acetate dissolved in 5.00 g of trifluoroacetic acid. After being connected to the gas manifold, the reactor was purged several times with helium at 1000 psig (6.89 MPa), followed by several purges of methane with a final methane pressure of 800 psig (5.52 MPa), and isolated from the gas manifold.

When ¹³CH₄ was used, the reactor was immersed in a liquid nitrogen bath after being purged with helium. When the temperature had reached -190°C, the reactor was connected to a mechanical vacuum pump and evacuated. The reactor was then isolated from the vacuum pump and, while still immersed in liquid nitrogen, was connected to the cylinders of ¹³CH₄ to allow transfer of the cylinders' contents to the reactor. After transfer of the cylinder's contents, the reactor was sealed and placed in a silicone oil bath. The ¹³CH₄, specified by the supplier at 99% isotopic purity, was supplied in 1-L cylinders at 20 psig (0.14 MPa) pressure. The contents of two cylinders were required to obtain the necessary >800 psig (5.52 MPa) pressure for reaction.

When necessary, the gases were dried prior to entering the reactor by passing through an 8-ft (2.44-m) x 1/4-in (0.64-cm) coil of stainless-steel tubing immersed in an acetone/dry ice bath.

The reactor was heated in a bath of silicone oil at 80°C for 5 days. The reactor pressure was monitored by a pressure transducer and recorded during the run. Blank runs followed the same procedure with the exception of helium replacing methane.

Upon completion of the run, the reactor was depressurized and the liquid was removed for analysis. After removal of the reactor's liquid contents, the reactor was filled with deionized water, capped, and placed in a 720-W ultrasonic cleaner for one hour. This procedure loosened the palladium metal

which formed during the reaction. The solution was then passed through a preweighed 0.50- μ m Teflon® filter and air dried. The residue on the filter was removed and identified by SEM and EDS. Gaseous components were analyzed on a Hewlett-Packard 5730 gas chromatograph. Liquid samples were analyzed on a Hewlett-Packard 5988A GC/MS system.

RESULTS AND DISCUSSION The results reported by Sen and coworkers were reproduced (Run 241); production of methyl trifluoroacetate was observed and a fine metallic powder was recovered. SEM and EDS analysis of the powder confirmed it to be palladium metal with crystallites of the order of 1 μ m in size. Quantitative analysis of the palladium metal residue indicated >80% of the palladium acetate was recovered as palladium metal. Methane conversion, calculated by the difference in pressure from the beginning to the end of the run, was ~3 mol% (Table IV). Analysis of the reaction mixture from Run 241 identified several other oxygenated compounds and water. To determine the source of these compounds, the palladium(II) acetate dissolved in trifluoroacetic acid for Run 242 was analyzed prior to introduction of methane. This revealed the presence of methyl trifluoroacetate, the product of methane oxidation, prior to introduction of methane, and the same components identified before.

The trifluoroacetic acid was analyzed to determine if the methyl trifluoroacetate and other compounds found in Runs 241 and 242 were present. All the unexpected compounds except methyl trifluoroacetate were detected, including a significant quantity of water. A blank run was conducted in which the methane was replaced with helium at 800 psig (5.52 MPa). All reaction conditions and operations were identical to previous runs. This experiment resulted in the production of methyl trifluoroacetate and a 68.30% recovery of palladium metal. The only logical origin of the methyl group of the ester is via decomposition of the acetate ligand of the starting material.

The gas in the reactor was sampled prior to venting and recovery of liquid products. Analysis of the gas samples by high-resolution gas chromatography, after completion of the experiments, showed only the components present in the feed gas.

For use in the remaining experiments, dry, high-purity trifluoroacetic acid was obtained in sealed ampules containing enough acid for a single use. Analysis of this trifluoroacetic acid revealed no detectable quantities of water or other impurities previously detected. The blank run was repeated. After 150 hours at 80°C and 800 psig (5.52 MPa) helium, the reactor was opened and the solution removed for analysis and comparison with the starting material. No difference in composition was detected between the two samples. Water (8 x 10⁻³ moles, a 10 fold excess) was then added to the mixture of Run 244, the reactor was charged with helium at 800 psig (5.52 MPa), and held at 80°C for 150 hours. Analysis of the products of reaction (Run 245) revealed the presence of methyl trifluoroacetate and methyl acetate. Since no methane was present in the system, the only source of the methyl group in the products is from the displaced acetate. This observation is inconsistent with that of Sen⁹ in that he did not observe any deuterium incorporation into the methyl trifluoroacetate when Pd(O₂CCD₃)₂ was used.

The first experiment (Run 246) to use both methane and the dry, high purity trifluoroacetic acid resulted in products similar to previous experiments with the exception that the amount of palladium metal recovered was only 39.20 mol%, a reduction of >50%. We attribute this decrease to the absence of side reactions caused by the water in the trifluoroacetic acid.

To determine if any methane from the gas phase was involved in the reaction, an experiment (Run 248) was conducted using methane that was isotopically enriched in carbon-13. Oxidation products arising solely from the labelled methane, determined by GC-MS, would eliminate the possibility of products arising from the acetate ligand on the palladium(II) acetate. The reactor was filled as described above. Operating under conditions similar to previous experiments resulted in similar methane conversions but a recovered palladium metal amount of only 7.88 mol%. Analysis of the product mixture revealed both CF₃C(O)O¹³CH₃ and CF₃C(O)OCH₃. Single Ion Monitoring (SIM) analysis of the isotopic ratio of the labeled products gave a ¹³C/¹²C ratio of 4.98. The composition of the labeled methane was determined by mass spectroscopy to be 93.5% ¹³CH₄ and 6.5% ¹²CH₄, a ratio of 14.38. This means that ~1% of the methyl carbon in the methyl trifluoroacetate comes from a source other than the labeled methane. This confirms our postulate that not all of the product arises from the methane introduced as a reactant.

To test the postulate that the presence of water in the reactor system was responsible for the observed decrease in palladium metal recovery, three experiments were conducted (Runs 250, 252, and 254) in which the gases were dried prior to entering the reactor as described above. The reactor was prepared as in the ¹³CH₄ experiment. After warming to room temperature, 4.8 x 10⁻³ g (2.7 x 10⁻⁴ moles) of water was recovered from the drying trap. The result of these experiments is that the methane consumption and product distribution remained the same as previously observed, but recovery of palladium metal was only 4.21, 7.46, and 8.29 mol%, respectively. This suggests that the presence of water in either the reactants or in the reactor system is responsible for the greater quantities of palladium metal reported in the literature. Water was not detected in the product mixture by GC/MS for these experiments. Quantitation of reaction products for Run 254 revealed that 0.13 weight percent of the product is methyl trifluoroacetate. This corresponds to a conversion of reactants to the desired product of 0.8%.

Sen and coworkers postulated that the mechanism of this reaction is electrophilic attack on the methane by Pd(II), followed by reductive elimination to give Pd metal and the alcohol derivative. This mechanism is supported only by

the fact that palladium is a strong electrophile and a good two electron oxidant. Our observations do not support the original assumption that the reaction, as stated in Equation 1, is a 1:1 stoichiometric reaction between methane and palladium(II) trifluoroacetate. Table IV lists the molar balance for the experiments. The sixth column of the table shows the ratio of methane consumed to palladium metal recovered. The data from the early experiments, when water was present, show that the molar ratio of methane consumed to palladium metal recovered is of the order of 10. In later experiments, when water was removed from the reactants, this ratio is an order of magnitude larger.

These inconsistencies leave open the important questions about the reaction mechanism which is key to proper evaluation of this reaction as a method for direct oxidation of methane. If the methane is being consumed by some other reaction not involving palladium, is the palladium(0) being reoxidized to a palladium(II) complex, or are other impurities present in the system?

CONCLUSION

This brief study may lead to the conclusion that ample opportunity exists to improve the OHC catalyst used in the first step of the PETC Methane-to-Higher Hydrocarbon Process and, accordingly, improve the entire process. Due to regulations limiting the aromatic and chlorine content of gasoline, the chloromethane conversion reaction will need to be fine tuned before commercial consideration. Chloromethane, a high-valued intermediate, may be the choice of product in this reaction scheme.

The study involving organometallics has shown that the reaction expressed in Equation 1 does occur, as confirmed by the production of $\text{CF}_3\text{CO}_2^{13}\text{CH}_3$ from $^{13}\text{CH}_4$, but that this reaction is not responsible for all product methyl trifluoroacetate. When a blank experiment was performed using the highest purity starting materials and replacing methane with helium, methyl trifluoroacetate was detected in the product if water was not excluded from the system. The presence of water in the reaction mixture appears to cause the palladium acetate/trifluoroacetate complex to decompose and produce methyl trifluoroacetate and account for the high yields of palladium metal reported in the literature.

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DISCLAIMER

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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TABLE I CONSTITUENTS BY WEIGHT

CATALYST	% METAL CHLORIDE	% SiO_2	% KCl	% LaCl_3
Cu	41.66	37.50	11.46	9.38
Co	55.17	28.82	8.81	7.20
Ni	58.46	26.70	8.16	6.68
Pb	66.96	21.24	6.49	5.31
Ag	44.73	35.53	10.86	8.88
Pt	41.66	37.50	11.46	9.38
Cr	56.24	28.12	8.61	7.03
Blank	00.00	64.29	19.64	16.07

TABLE II REACTANT CONVERSION
3.0 GRAMS CATALYST, RESIDENCE TIME 8.3 SECONDS, TEMP. 340°C,
FLOWS CH₄ = HCl = 4.0 mL/MIN, O₂ = N₂ = 2.0 mL/MIN

CATALYST	% CH ₄ CONV.	% HCl CONV.	% O ₂ CONV.
Cu	47.69	80.08	83.86
Co	61.03	52.54	85.48
Ni	19.31	19.81	11.11
Pb	5.51	14.86	9.41
Ag	4.54	7.95	14.03
Pt ^a	54.34	0.01	3.10
Pt ^b	7.36	3.29	6.56
Cr	13.15	3.54	33.21
Blank	16.16	6.63	25.31

^aAfter 24 hours on stream

^bAfter 48 hours on stream

TABLE III NORMALIZED CARBON PRODUCT DISTRIBUTION
3.0 GRAMS CATALYST, RESIDENCE TIME 8.3 SECONDS, TEMP. 340°C,
FLOWS CH₄ = HCl = 4.0 mL/MIN, O₂ = N₂ = 2.0 mL/MIN

CATALYST	CH ₃ Cl	CH ₂ Cl ₂	CHCl ₃	CCl ₄	CO	CO ₂	HCOOH
Cu	30.03	39.42	9.39	0.14	0.00	12.44	8.58
Co	44.31	12.44	1.32	1.32	0.00	3.67	38.26
Ni	23.03	3.78	0.00	0.00	0.00	0.00	73.19
Pb	20.97	3.49	0.37	0.37	0.00	0.00	75.17
Ag	12.71	1.37	0.09	0.09	0.00	14.52	71.31
Pt ^a	31.26	3.49	0.30	0.18	0.00	17.35	47.42
Pt ^b	28.96	3.28	0.42	0.14	0.00	10.75	56.45
Cr	10.92	2.66	0.60	0.00	64.77	21.05	0.00
Blank	10.01	0.45	0.09	0.00	69.55	7.02	12.78

^aAfter 24 hours on stream

^bAfter 48 hours on stream

TABLE IV ORGANOMETALLIC METHANE OXIDATION RESULTS

RUN	MOL % Pd METAL FORMED	MOL % CH ₄ CONSUMED	MOLES Pd METAL FORMED (X10 ⁴)	MOLES CH ₄ CONSUMED (X10 ³)	MOLES CH ₄ MOLES Pd	% CH ₄ CONVERTED TO CF ₃ C(O)OCH ₃
241	83.50	3.00	4.70	4.69	9.98	
242	77.00	3.13	5.14	3.59	6.99	
243	68.30	N/A	4.30	0.00	N/A	
244	0.00	N/A	0.00	N/A	N/A	
245	83.20	N/A	5.76	0.00	N/A	
246	39.20	6.42	2.72	4.54	16.72	0.4
248	7.88	4.08	0.55	3.07	56.32	
250	4.21	4.01	0.29	5.94	203.84	
252	7.46	10.30	0.49	6.90	141.15	
254	8.29	9.87	0.55	8.44	153.45	0.8